<International Research Center for Elements Science>Advanced Solid State Chemistry

International Research Center for Elements Science – Advanced Solid State Chemistry –

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Prof
SHIMAKAWA, Yuichi
(D Sc)

Assoc Prof
KAN, Daisuke
(D Sc)

Assist Prof
SAITO, Takashi
(D Sc)

Program-Specific Assist Prof
ICHIKAWA, Noriya
(D Eng)

PD (JPSJ)
FABIO, Denis Romero
(Ph D)

Students

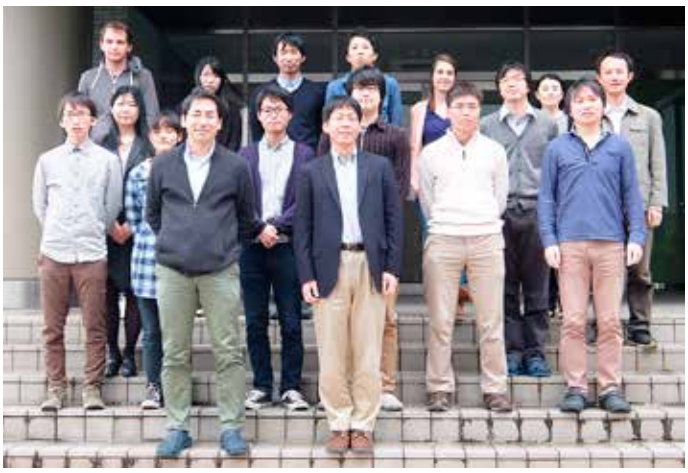
SEKI, Hayato (D3)
HOSAKA, Yoshiteru (D2)
GUO, Haichuan (D2)
XIONG, Peng (D1)
SASAKI, Takahiro (M2)
BABA, Erina (M2)
OZAKI, Yusuke (M1)
NISHIMURA, Tomoe (M1)
WADA, Tamaki (M1)

Scope of Research

Transition metal oxides have a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides are used in current electronic devices. Our research mainly focuses on perovskite-structured transition metal oxides with novel functional properties due to complex couplings between their lattices, charges and spins. We are currently exploring such functional oxides with advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth.

KEYWORDS

Solid State Chemistry
Functional Transition Metal Oxides
Epitaxial Thin Film Growth
High Pressure Synthesis
Perovskite Structured Oxides



Selected Publications

Hosaka, Y.; Ichikawa, N.; Saito, T.; Manuel, P.; Khalyavin, D.; Attfield, J. P.; Shimakawa, Y., Two-dimensional Charge Disproportionation of the Unusual High-valence State Fe^{4+} in a Layered Double Perovskite, *J. Am. Chem. Soc.*, **137,** 7468-7473 (2015).

Chen, W.-T.; Mizumaki, M.; Seki, H.; Senn, M.; Saito, T.; Kan, D.; Attfield, J. P.; Shimakawa, Y., A Half-metallic A- and B-Site-ordered Quadruple Perovskite Oxide $CaCu_3Fe_2Re_2O_{12}$ with Large Magnetization and a High Transition Temperature, *Nat. Comm.*, **5,** [3909-1]-[3909-7] (2014).

Matsumoto, K.; Haruta, M.; Kawai, M.; Sakaiguchi, A.; Ichikawa, N.; Kurata, H.; Shimakawa, Y., Selective Reduction of Layers at Low Temperature in Artificial Superlattice Thin Films, *Sci. Rep.*, **1,** [27-1]-[27-14] (2011).

Inoue, S.; Kawai, M.; Ichikawa, N.; Kageyama, H.; Paulus, W.; Shimakawa, Y., Anisotropic Oxygen Diffusion at Low Temperature in Perovskite-structure Iron Oxides, *Nat. Chem.*, **2,** 213-217 (2010).

Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y., Temperature-induced A-B Intersite Charge Transfer in an A-Site-ordered $LaCu_3Fe_4O_{12}$ Perovskite, *Nature*, **458,** 60-63 (2009).

Two-dimensional Charge Disproportionation of the Unusual High Valence State Fe^{4+} in a Layered Double Perovskite

Many iron oxides contain Fe^{2+} or Fe^{3+} because these oxidation states are very stable in octahedral and tetrahedral oxygen coordination. In the simple perovskite $AFe^{4+}O_3$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) synthesized under strongly oxidizing conditions, however, unusual high oxidation states of Fe like Fe^{4+} can be stabilized. The low-lying Fe-3d orbitals strongly hybridize with O-2p orbitals, and as a result, oxygen p holes (ligand holes, *L*) are produced in the electronic structure of the perovskites. These ligand holes are the reason that Fe^{4+}, which is expected to have $t_{2g}^3e_g^1$ electron configuration, does not induce Jahn–Teller distortion like the isoelectronic Mn^{3+} does. The ligand holes are mobile at high temperatures, leading to metallic conduction, but often become unstable at low temperatures. The instability of the high oxidation state of Fe^{4+} is relieved by charge disproportionation (CD) from Fe^{4+} to Fe^{3+} and Fe^{5+}. In the ground state, the ligand holes are localized alternately at the Fe sites, and the CD transition ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$) can be described as $2d^5\underline{L} \rightarrow d^5 + d^5\underline{L}^2$.

In this paper, we investigated the CD and magnetic transition behaviors in the newly discovered layered double-perovskite Ca_2FeMnO_6 with a two-dimensional arrangement containing high valence Fe^{4+} at room temperature. The new compound, Ca_2FeMnO_6, is a fully oxygenated double perovskite Ca_2FeMnO_6 with a layered arrangement of $Fe^{4+}O_6$ and $Mn^{4+}O_6$ octahedra (Figure 1) and is the first compound that has an isolated two-dimensional layered arrangement of high valent Fe^{4+}. This oxide was obtained by low-temperature topochemical oxidation of the brownmillerite Ca_2FeMnO_5. Our analysis of the low-temperature neutron diffraction patterns revealed that below 95 K, the charge-disproportionated Fe^{3+} and Fe^{5+} are ordered in a checkerboard pattern in the two-dimensional FeO_6 octahedral layers and the checkerboard-type layers stack in an in-phase manner. Two-dimensional localization of the ligand holes with effective spins plays an important role in the noncollinear magnetic structure of Ca_2FeMnO_6.

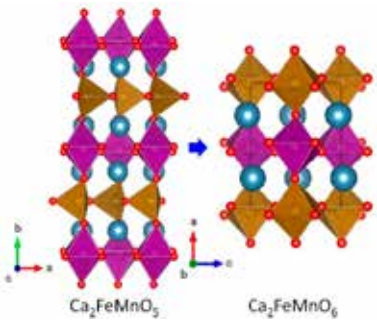


Figure 1. Crystal structure of layered double perovskite Ca_2FeMnO_6 (right) obtained by topochemical oxidation of brownmillerite $CaFe_2MnO_5$ (left) at a low temperature. Blue, brown, purple, and red spheres represent Ca, Fe, Mn, and O ions, respectively.

Significant Strain-induced Increase in Metal–Insulator Transition Temperature in Oxygen-deficient Fe Oxide Epitaxial Thin Films

Transition-metal oxide epitaxial thin films, which often exhibit behaviors different from those of the bulk oxide, have attracted a great deal of attention as a platform for exploring novel functionalities. This is in part because strong correlations between charges, spins, and lattices determine the functional properties of the films, and these correlations are affected by structural distortions from substrate-induced strain effects. While these strain effects have been studied in many fully oxygenated oxides, such as ABO_3 perovskites, those in oxygen-deficient oxides consisting of various oxygen coordination environments like tetrahedra and pyramids as well as octahedra remain unexplored. Substrate-induced modifications of such various oxygen coordination units would provide additional routes to controlling the strong correlations and consequently to modifying or even enhancing the functional properties.

We focused here on oxygen-deficient Fe-based perovskite oxides, $SrFeO_x$ (SFOx), which exhibit a variety of structural and physical properties, depending on their oxygen vacancy concentration, and discovered that an oxygen-deficient $SrFeO_x$ (x~2.8) epitaxial thin film shows a transport behavior markedly different from the corresponding behavior in the bulk material. The present thin film under substrate-induced tensile strain shows a metal-insulator transition associated with charge disproportionation of $Fe^{3.66+}$ into Fe^{4+} and Fe^{3+} at 620 K. This transition temperature is much higher than the 70 K reported for the transition in the bulk material and is also much higher than room temperature. We also found the transition to be accompanied by oxygen-vacancy ordering. This significant increase in the metal-insulator transition temperature demonstrates that epitaxial growth of oxygen-deficient oxides under substrate-induced strain is a promising route for exploring novel functionality.

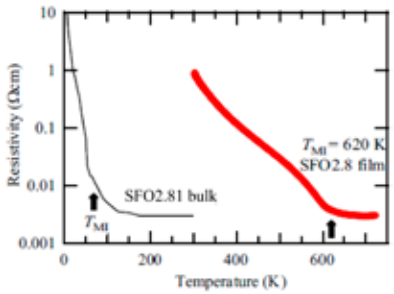


Figure 2. Temperature dependence of the electrical resistivity of SFO2.8 film from 720 to 300 K in air (red line) and $SrFeO_x$ (x ~ 2.81) bulk from 300 to 5 K (black line). The arrows denote the metal-insulator transition temperatures (T_{MI}). The resistivity data of the SFO2.81 bulk were taken from a report by P. Adler et al. (*Phys. Rev. B*, **73**, 094451 (2006)).